

COATINGS

UDC 666.1:546.841

OBTAINING SOL-GEL BY MEANS OF INDIUM OXIDE THIN FILMS WITH ADDED TIN ON GLASS SUBSTRATES

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Translated from *Steklo i Keramika*, No. 12, pp. 8 – 12, December, 2013.

The sol-gel method was used to obtain from a film forming solution, based on $\text{In}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and acetylacetone, thin-film materials $\text{In}_2\text{O}_3\text{-Sn}$, characterized by transmittance 65 – 83% at wavelengths 450 – 800 nm, on glass substrates. IR and UV spectroscopy and viscometry were used to determine the composition of the film forming solution (solvated oligomers $-\text{In}(\text{Hacac})_n-\text{O}-\text{In}(\text{Hacac})_n-\text{O}-\text{Sn}(\text{Hacac})_m-\text{O}-\text{In}(\text{Hacac})_n-\text{O}-$) and the processes resulting in the formation of the solution. Thermal analysis was used to determine the synthesis temperature regime for the $\text{In}_2\text{O}_3\text{-Sn}$ films. It was determined that tin (IV), which forms after thermal destruction of a complex tin (II) particle with acetylacetone and oxidation of SnO to SnO_2 , predominates in the oxide phase.

Key words: sol-gel method, film-forming solution, thin film.

Thin films of indium oxide (III) with tin (IV) additions on glass substrates possess good transmittance and high conductivity, as a result of which such films are widely used in the production of transparent, electrically conducting, heat reflective coatings and gas-sensitive materials [1 – 3]. The existing methods of obtaining such films — cathode magnetron sputtering, pulverization and so on [4, 5] — are energy intensive and the coatings obtained do not always have the required properties. The sol-gel technology, widely used for obtaining thin-film oxide materials from film forming solutions (FFS), makes it possible to use precursors in a dissolved form, where the doping component is distributed uniformly in the matrix of the main film-forming material. This confers a number of advantages, such as uniformity of the final material and the possibility of controlling the structure and composition of the thin films at all stages of the process [6]. However, the question of the mechanism of restructuring in FFS is complicated and little studied. Meanwhile, in practice it is necessary to know how the physical and chemical laws determining the flow of chemical processes at the time the films are obtained affect the structure and properties of the material obtained. For this reason, the present work is focused on obtaining thin-film materials $\text{In}_2\text{O}_3\text{-Sn}$ on glass substrates by the sol-gel method, studying the physical and

chemical processes leading to the formation of the films and studying their surface morphology and properties.

The thin films were synthesized from film forming solutions by the sol-gel method. These solutions were prepared by dissolving in 96% ethanol $\text{In}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and acetylacetone (Hacac), which is the first film-forming solution FFS-1, and $\text{In}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$, SnCl_4 and acetylacetone (Hacac), which is the second film-forming solution FFS-2, at room temperature. The concentrations of the substances in solution were as follows: $C(\text{In}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}) = 0.3 - 0.03$ mol/liter; $C(\text{SnCl}_2 \cdot 2\text{H}_2\text{O}) = 0.03 - 0.3$ mol/liter; $C(\text{SnCl}_4) = 0.03 - 0.3$ mol/liter; $C(\text{Hacac}) = 0.3$ mol/liter. A concentrated solution of hydrochloric acid was added in amounts to 0.2 mol/liter to the FFS to increase the solubility of tin (IV, II) chlorides and suppress the hydrolysis of the salts. The composition of the film-forming solution was investigated by IR and UV spectroscopy. An IKS-29 spectrophotometer was used to obtain the IR spectra in the wave number range 400 – 4200 cm^{-1} and an SF-20 spectrophotometer was used to obtain the UV spectra in the wavelength range 220 – 340 nm relative to the solvent ethanol of the FFS. The frequencies were compared with the published data [7 – 9]. Viscometry data obtained on a VPZH-2 viscometer with 0.99 mm in diameter capillary was used to determine the film forming capacity of the solutions. The rate constant of the reaction occurring in the solutions was calculated from

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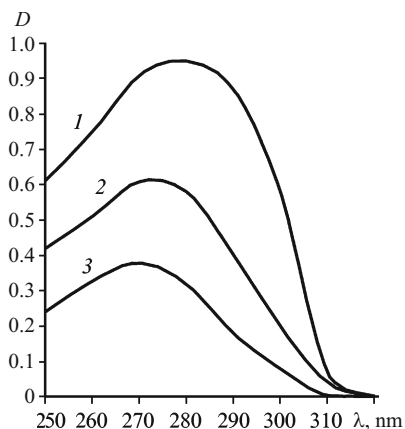


Fig. 1. Absorption in the UV range: 1) acidified solution of Hacac in ethanol; 2) FFS-1; 3) FFS-2.

the relation $\ln \eta_{sp} = \alpha + \kappa \tau$ [10] derived under the following assumptions: the viscosity of the system increases with increasing content of the reaction product, the Staudinger equation holds [11] and the hydrolysis and polycondensation reactions occurring at the initial stage formally follow first-order kinetics.

The thin-film materials $\text{In}_2\text{O}_3\text{-Sn}$ (5–20%³) were obtained on glass substrates by pulling from film forming solutions at the rate 2 mm/sec. After preliminary drying the samples were heat treated in a muffle furnace at temperature 873 K with heating rate 14 K/min. The samples were annealed at a temperature based on thermal analysis performed in air using a simultaneous STA 449 thermal analyzer.

The composition of the oxide films was determined by x-ray phase analysis performed with a DRON-3M diffractometer (CuK_α radiation, Ni filter). The index of refraction and thickness of the film were measured with an LÉF-3M laser ellipsometer and the surface resistance with a VKS-9 voltmeter. An IKS-3 spectrophotometer was used to measure the transmittance of the films in the visible range.

A HITACHI TM-3000 scanning electron microscope was used to investigate the surface morphology. The UV ab-

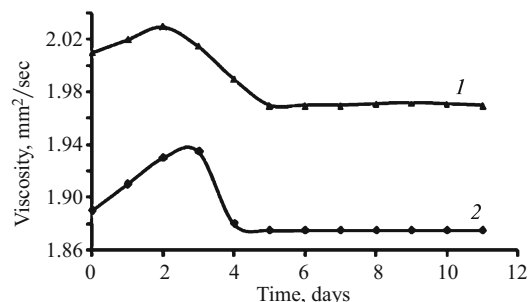


Fig. 2. Temporal variation of the viscosity of solutions: 1) FFS-1; 2) FFS-2.

sorption edges of $\text{In}_2\text{O}_3\text{-Sn}$ films on quartz substrates were determined from spectra obtained with a Specord M-40 spectrophotometer at wavelengths 200–900 nm. The needle-scratch method was used to determine the adhesion.

A comparative analysis of the IR spectra of the FFS as well as a solution of Hacac in ethanol (Table 1) shows the formation of a chemical bond between Hacac and In^{3+} cations. The vibrations of the characteristic group In-O at 510 cm^{-1} and a shift in the vibrations of the Hacac bonds were recorded in the IR spectra of FFS-1 and -2. Since the vibrations of the Sn-O bonds lie at lower frequencies (260 cm^{-1}), which are not recorded by IKS-29, the formation of a complex particle of $\text{Sn}^{2+(4+)}$ with Hacac was not investigated. However, it is known from published data [12] that a complex particle comprised of Sn^{2+} and Hacac forms preferably in the undissociated enol form.

The presence of absorption of the diffuse band of an OH group at 3300 cm^{-1} (FFS-1) and 3315 cm^{-1} (FFS-2) as well as absorption near 1543 cm^{-1} (FFS-1) and 1534 cm^{-1} (FFS-2), pertaining to the vibrations of the $(\text{C-O})+(\text{C-C})$ bonds of a chelate, attest to the existence in FFS of the undissociated enol form of Hacac. The vibrations of the (C=O) bond at 1652 cm^{-1} (FFS-1) and 1646 cm^{-1} (FFS-2) indicate the presence in FFS of the undissociated enol form of Hacac and ketone form of Hacac. The UV transmission spectra of FFS (Fig. 1) have one wide absorption band at $\lambda = 270\text{--}275 \text{ nm}$ due to $\pi\text{-}\pi^*$ transitions. According to the published data [9] this region of absorption also characterizes a keto-enol equilibrium of Hacac, where the enol form of the latter is undissociated. According to all experimental data taken together and taking account of the fact that the salts of tin (II, IV) and indium (III) are subjected to hydrolysis in the 96% ethanol solution, it can be supposed that the experimental film forming solutions are solutions of the complex particles $[\text{InOH}(\text{Hacac})_n]^{3+}$ and $[\text{SnOH}(\text{Hacac})_m]^{2+(4+)}$.

Viscosity serves as a criterion for the film-forming capacity of solutions as well as their temporal stability. The values of the kinematic viscosity η confirm the film-forming capacity of the experimental FFS ($\eta = (1.890\text{--}2.010) \pm 0.004 \text{ mm}^2/\text{sec}$) [13]. According to Fig. 2 stable film formation is reached after the solution has been kept at room tem-

³ Here and below, the elemental content, %.

TABLE 1. Main Characteristic Vibrations in the IR region of the Spectrum of a Solution of Hacac in Ethanol, FFS-1, FFS-2

Frequency assignment	ν, cm^{-1} Hacac	ν, cm^{-1} POR-1	ν, cm^{-1} POR-2
–OH	3560 – 2750	3300	3315
–CO–C=C–OH	1735	–	–
C=O	–	1652	1646
C–O + C–C (chelate)	1514	1543	1534
C–C + C–O	1197	1060	1053
$\pi(\text{C-H})$	812	795	891
In–O	–	510	510

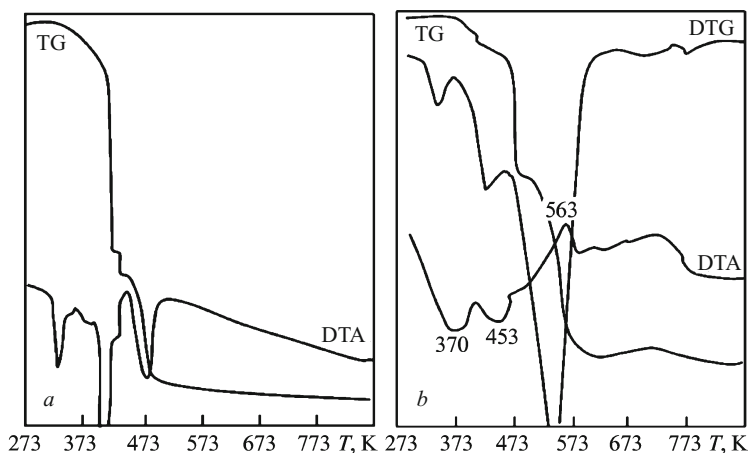


Fig. 3. Decomposition thermograms: *a*) $\text{In}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$; *b*) dried FFS-1.

perature for 5 days. Analysis of the kinematic information obtained from the variation of the specific viscosity of the solutions during the first 3 days of curing of the FFS indicates quite low values of the rate constant of the process $k_v = 10^{-5} \text{ sec}^{-1}$ (the rate constant for the hydrolysis of indium and tin salts is much higher), which suggests that the process of formation of a FFS reaches a limiting stage during the first three days of the polycondensation reaction. It should also be noted that the rate constant is almost independent of the composition of the FFS. The values are $(2.5 \pm 0.5) \cdot 10^{-5} \text{ sec}^{-1}$ for FFS-1 and $(3.2 \pm 0.3) \cdot 10^{-5} \text{ sec}^{-1}$ for FFS-2. The reduction of viscosity before it stabilizes can be explained only by a restructuring of the solvent and the oligomer formed in the FFS [10]. Thus, on the basis of the indicated studies it can be supposed that FFS deposited on a substrate in the stable region of film formation ($\eta = \text{const}$) comprise solvate oligomers $-\text{In}(\text{Hacac})_n-\text{O}-\text{In}(\text{Hacac})_n-\text{O}-\text{Sn}(\text{Hacac})_m-\text{O}-\text{In}(\text{Hacac})_n-\text{O}-$.

After being deposited on a glass substrate FFS were heat treated at 333 K to increase adhesion and remove the solvent. According to thermal analysis $\text{In}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ (Fig. 3*a*) and the dried ethanol solution of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ with Hacac (Fig. 3*b*) the FFS-1 and -2 start to decompose above this temperature. The decomposition thermograms show that the decomposition process consists of several stages. At the first stage the thermograms of the dried ethanol solution of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ with Hacac two endothermic effects are ob-

served in the temperature range 323 – 473 K; these effects possibly reflect the evaporation of the ethyl alcohol and adsorbed water molecules. The second stage ($T = 473 - 593 \text{ K}$) of decomposition is accompanied by an exothermal effect and corresponds to the decomposition of tin complexes (II) by removal of acetylacetone and its oxidation by the oxygen present in air.

This supposition also agrees with the published data [12], where it is shown that the complex compound $\text{SnHacacCl}_2 \cdot 2\text{H}_2\text{O}$ decomposes. At the third stage ($T = 593 - 873 \text{ K}$) a mass increase is observed on the TG curve; this could be associated with the oxidation of tin (II) and the formation of SnO_2 . The decomposition thermogram for indium nitrate (III) crystal hydrate is characterized by three endothermic effects peaking at 314, 393 and 483 K. The decomposition process for salt is already complete at 573 K. Thus, it is evident from thermal analysis that in order to obtain In_2O_3 -Sn films on glass substrates the samples must be annealed at temperature 873 K, at which the formation of indium oxide (III) and tin oxide (IV) is complete.

According to x-ray phase analysis, the samples annealed at the temperature indicated above comprise a solid solution based on In_2O_3 . The phase is identified on the basis of the diffraction peaks with interplane distances 4.16, 2.92, 2.53, 2.15, 1.97, 1.79 and 1.64 Å. Semiconducting films In_2O_3 :Sn with good adhesion, which increases with increasing Sn content, are obtained under these conditions (Tables 2 and 3).

TABLE 2. Physical Properties of In_2O_3 -Sn Films Obtained from FFS-1

Sn, %	1 layer					2 layers				
	$R, \text{k}\Omega$	$n \pm 0.06$	$d \pm 0.9, \text{nm}$	$F \pm 0.02, \text{kg/mm}^2$	$\lambda_{\text{edge}}^*, \text{nm}$	$R, \text{k}\Omega$	$n \pm 0.03$	$d \pm 0.5, \text{nm}$	$F \pm 0.02, \text{kg/mm}^2$	$\lambda_{\text{edge}}^*, \text{nm}$
5	$10^2 - 10^3$	1.63	—	0.11	324	1 – 8	—	168.7	0.15	—
10	$10^2 - 10^3$	1.70	82.9	—	—	1 – 6	1.81	143.4	0.24	—
15	$1 - 10^3$	1.73	107.1	0.15	325	1 – 3	1.80	152.9	0.24	340
20	$1 - 10^3$	1.74	110.8	0.46	317	1 – 10	1.92	123.0	0.31	327

* Absorption.

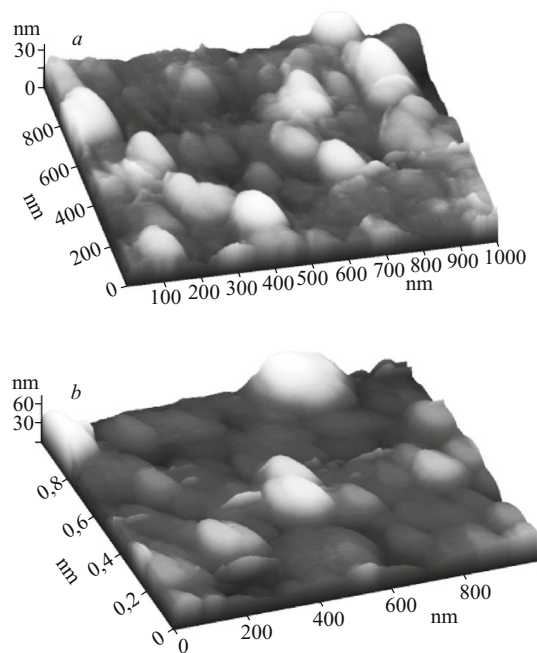


Fig. 4. Surface morphology of $\text{In}_2\text{O}_3\text{-Sn}$ films (15% elemental Sn content): *a*) from FFS-1; *b*) from FFS-2.

In_2O_3 films without Sn have more adhesion and can be easily removed by pressing. They are opaque in the visible range of the spectrum. The addition of 5% in $\text{In}_2\text{O}_3\text{-Sn}$ gives high-impedance cloudy films. A transparent coating is obtained only by increasing the Sn content in them.

Comparing the properties of one- and two-layer films (see Tables 2 and 3) it is evident that after the second deposition the resistance along the surface of the films stabilizes and decreases.

As the number of layers increases, the thickness and therefore the size of the crystallite increase. They increase as new portions of the FSS arrive and larger crystallites replace smaller ones; the morphology of the surface changes. As a result the number of charge carriers and the conductivity increase. The thickness of the films and the impedance increase not only with the number of layers deposited but also with increasing Sn content in the In_2O_3 film. This change in the impedance could also be associated with the fact that the

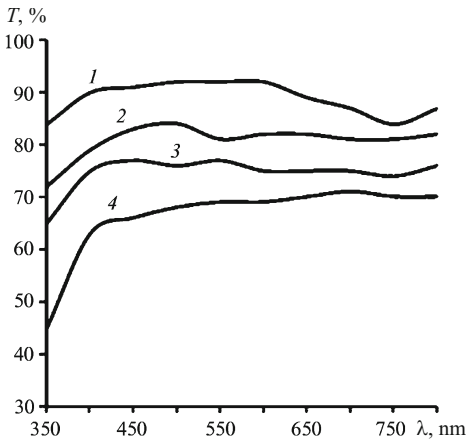


Fig. 5. Visible range transmission spectrum of films: *a*) glass slide; *b*) $\text{In}_2\text{O}_3\text{-Sn}$ (elemental content Sn 10%) from FFS-1; *c*) $\text{In}_2\text{O}_3\text{-Sn}$ (elemental content Sn 10%) from FFS-2; *d*) $\text{In}_2\text{O}_3\text{-Sn}$ (elemental content Sn 15%) from FFS-1.

conductivity of tin oxide (IV) is higher than that of indium oxide (III) [14]. The refractive index also increases with increasing thickness of these films. The largest shift of the edge of the absorption band of the films in the UV region compared with a glass substrate is observed for films with elemental Sn content in the range 15 – 20%. The FFS-1 with the low-charge cation Sn^{2+} makes it possible to obtain films with higher conductivity. Since the surface morphology of these samples is similar to that of films obtained from FFS-2 (Fig. 4), this can be explained by the fact that during the heat-treatment of FFS-1 a disproportionation reaction of Sn^{2+} occurs with the formation of impurity metallic tin, which increases the conductivity of the films [15].

The visible-range spectral characteristics of the $\text{In}_2\text{O}_3\text{-Sn}$ films obtained from FFS-1 differ as a function of the tin content. As Fig. 5 shows, the transmission coefficient of glass with a film is lower than that of pure glass. The $\text{In}_2\text{O}_3\text{-Sn}$ (10%) film has the highest transmission coefficient.

CONCLUSIONS

In summary, $\text{In}_2\text{O}_3\text{-Sn}$ films (with elemental content 5 – 20%) on glass substrates were obtained by the sol-gel

TABLE 3. Physical Properties of $\text{In}_2\text{O}_3\text{-Sn}$ Films Obtained from FFS-2

Sn, %	1 layer					2 layers				
	<i>R</i> , kΩ	<i>n</i> ± 0.06	<i>d</i> ± 0.9, nm	<i>F</i> ± 0.02, kg/mm ²	<i>λ</i> _{edge} [*] , nm	<i>R</i> , kΩ	<i>n</i> ± 0.03	<i>d</i> ± 0.5, nm	<i>F</i> ± 0.02, kg/mm ²	<i>λ</i> _{edge} [*] , nm
5	∞	1.59	118.9	0.10	325	∞	1.60	160.7	0.11	–
10	∞	1.65	123.1	0.11	–	∞	1.72	173.1	0.14	–
15	∞	1.34	128.7	0.20	325	1 – 10 ³	1.79	169.5	0.24	342
20	1 – 10 ³	1.67	129.8	0.52	320	5 – 10 ³	1.76	162.3	0.56	327

* Absorption.

method from film forming solutions based on the complex compounds Hacac with Sn (II, IV) and In (III). The films obtained were characterized by transmittance 65 – 83% in the wavelength range 450 – 800 nm. The valence of tin in the FFS affects only the conductivity of the In_2O_3 –Sn films. The thin-film coatings obtained can be used as transparent electrodes for solar cells and LED. This will make it possible to increase the extraction efficiency for light generated by devices.

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